

A Comparison of Chilled DI Water/Ozone and CO₂-Based Supercritical Fluids as Replacements for Photoresist-Stripping Solvents

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Biography

Jim Rubin is a Technical Staff Member with the Supercritical Fluids Facility (SFF), within the Physical Organic Chemistry Group at Los Alamos. He received his Ph.D. in Materials Engineering from the New Mexico Institute of Mining and Technology in 1992. Leisa Davenhall is a Chemical Technician with the SFF, joining the Los Alamos staff in 1995. Jerome Barton was the Lead Technician of the SFF, retiring in May, 1998 after 20 years. Craig M.V. Taylor is the team leader of the SFF and is the Group Leader of the Physical Organic Chemistry Group.

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Abstract

Part of the Hewlett Packard Components Group's Product Stewardship program is the ongoing effort to investigate ways to eliminate or reduce as much as possible the use of chemical substances from manufacturing processes. Currently used techniques to remove hard-baked photoresists from semiconductor wafers require the use of inorganic chemicals or organic strippers and associated organic solvents. Environmental, health & safety, as well as cost considerations prompted the search for alternative, more environmentally-benign, and cost-effective solutions. Two promising, emerging technologies were selected for evaluation: The chilled DI water/ozone technique and supercritical fluids based on carbon dioxide (CO₂).

Evaluating chilled DI water/ozone shows this process to be effective for positive photoresist removal, but may not be compatible with all metallization systems. Testing of a closed-loop CO₂-based supercritical fluid process, known as **Supercritical CO₂ Resist Remover**, or SCORR, at Los Alamos, on behalf of Hewlett-Packard,

shows that this treatment process is effective in removing photoresists, and is fully compatible with commonly used metallization systems.

In this paper, we present details on the testing programs conducted with both the chilled DI H₂O/ozone and SCORR treatment processes.

Experimental - DI H₂O/Ozone

The SMS DIO3 TM photoresist strip process uses only chilled (5°C), deionized (DI) water and ozone instead of sulfuric acid/hydrogen peroxide or organic strippers/solvents.[1] The ozone reacts with the photoresist, breaking it down into CO₂ and oxygen. Since these breakdown products are gaseous, the hood exhaust removes them. The technique was developed by Robert Matthews, and is patented by Legacy Systems Inc. (Fremont, CA). SubMicron Systems Corporation (SMS) (Allentown, PA) and Universal Plastics (Santa Clara, CA) are licenced to use the technology in their wet stations.

As shown in Figure 1, the liquid flows from the process tank to the pump through a heat exchanger to the filter, through the ozonator and then back to the tank. The ozone is generated in the ozone generator and is fed to the ozonator where the ozone is mixed with the DI water. The gaseous ozone is also simultaneously fed to a diffusion plate in the bottom of the process tank. The gaseous ozone and the dissolved ozone in the DI water is being monitored using inline ozone analyzers.

The samples submitted to SMS to demonstrate the effectiveness of this process were: GaAs wafers, GaP wafers, Si wafers with Al metallizations, Si wafers with Ti-Pt metallizations, Si wafers with indium-tin (In-Sn) oxide metallization, and Si wafers with Ti-W metallization covered with positive photoresist (AZ 4330).

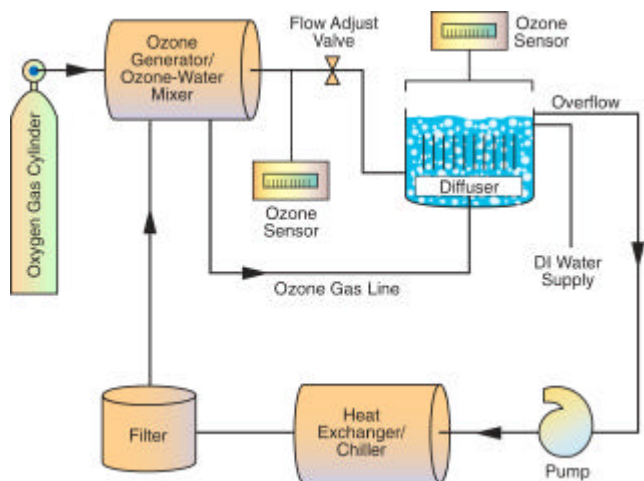


Figure 1. Schematic drawing of the SMS DIO3 photoresist-stripping system.

The resist-coated wafers, supported on a quartz boat, were submerged in the tank and subjected to the DIO3 process. The process time of 25 minutes was selected based on a stripping experiment result with a reference wafer that was covered with a 1.3-micron-thick photoresist layer. Since it was important to determine if any interactions between the metallizations and ozonated water would occur, a process time of 90 minutes was used to exaggerate any interactions. After the stripping process, the wafers were isopropyl alcohol dried in the SMS CLV dryer.

Results - DI H₂O/Ozone

After receiving the cleaned wafers back from SMS, the Scanning Electron Microscope (SEM) analysis and the FTIR surface analysis were performed by an independent testing lab. The process conditions, samples tested, and experimental results are listed in Table 1. The results confirm the absence of residual, positive photoresist material. Also, there were no adverse effects detected on the the above listed samples, except on the one with In-Sn oxide metallizations which showed signs of attack after the 90-minute exposure to the ozonated water.

EXPERIMENTAL - Supercritical CO₂

Supercritical fluids are used as solvents in many commercial applications, including the extraction of caffeine from coffee, fats from foods, and essential oils from plants for use in perfumes. The attractiveness of supercritical fluids as solvents stems from their unique combination of liquid-like and gas-like properties. A comparison is given in Table 2 of the diffusivity, viscosity and density of a typical organic fluid in the liquid state, gas state, and supercritical fluid state. To a first approximation,

Table 2. Comparison of physico-chemical properties of a typical organic fluid in the liquid, gas, and supercritical fluid state.

	Diffusivity (cm ² /s)	Viscosity (cP) or (mN·s/m ²)	Density (kg/m ³)
Liquid	10 ⁻⁵	1	1000
Supercritical Fluid	10 ⁻³	10 ⁻²	300
Gas	10 ⁻¹	10 ⁻²	1

the solvent power of a fluid is related to its density. The high, liquid-like densities achievable in supercritical fluids allows for substantial solubilities. Figure 2 shows the pressure-temperature-density surface for pure carbon dioxide. The critical point for pure CO₂, 304 K (31°C) and 7.39 MPa (1072 psi) is shown in Figure 2 by the solid circle. It can be seen that relatively small changes in temperature or pressure, above the critical values, can result in large changes in CO₂ density. It is this tunability of density which is one of the most attractive attributes of supercritical fluids. Also, the gas-like properties of low viscosity and high diffusivity provides for effective mass transport into granular and micro-porous matrices. Finally, the absence of surface tension provides for excellent surface wetting. Table 3 gives a comparison of several physico-chemical properties of carbon dioxide, as liquid and supercritical fluid, and several other commonly used liquid solvents.

Table 1. Test conditions, samples processed, and results obtained with the SMS DIO3 TM technique. (* Oxygen flow rate held constant at 3.5 liter/min at 20 psi).

Slot	Wafers + AZ 4330	Gas O ₂ (g/m ³)	Diss. O ₃ (g/m ³)	P _{ozone} * (psi)	T (°C)	Time (min.)	Remarks
1	Si wafer	268	85	20	5.2	90	Reference wafer for the process
2	GaP wafer	268	85.3	20	5.2	90	No adverse effects observed
3	GaAs wafer	272	86.1	20	5.1	90	No adverse effects observed
4	Si wafer + Ti-Pt	272	86.1	20	5.1	90	No adverse effects observed
5	Si wafer + Al	271	86	20	5.2	90	Resist gone, except at holder contact points at wafer edge
6	Si wafer + Ti-W	271	88.5	20	5.2	90	Resist gone, except at holder contact points at wafer edge. No visible attack on Ti-W
7	Si wafer + In-Sn oxide	271	88.5	20	5.1	90	Resist gone. The In-Sn oxide might have reacted.

Table 3. Physico-chemical properties of dense-phase carbon dioxide and other cleaning agents. (Typical values at ambient conditions unless otherwise stated.)

Solvent	Viscosity (cP) or (mN·s/m ²)	Surface tension (dynes/cm) or (mN/m)	Relative dielectric constant	Dipole moment (Debye)	Density (kg/m ³)
Liquid CO ₂	0.08 (@ 20°C, 105 atm)	1.5 (@ 20°C, boiling line)	1.6 (@ 0°C, 100 atm)	0	870 (@ 20°C, 105 atm)
Supercritical fluid CO ₂	0.03 (@ 35°C, 75 atm)	0 (above critical point)	1.3 (@ 35°C, 80 atm)	0	300 (@ 35°C, 75 atm)
1,1,1- trichloroethane	0.81	25.2	7.5	1.7	1300
methanol	0.54	22.1	32.7	1.7	800
water	1.00	72.0	78.5	1.8	1000

A recent article [2] has shown that pure, liquid propylene carbonate, (1,3-Dioxolane-2-one, 4-methyl; CAS # 108-32-7), hereafter referred to as PCO₃, as well as a 95/5 mixture of propylene carbonate and water, are effective, low-toxicity replacements for methylene chloride and methyl chloroform in the debonding of a negative,

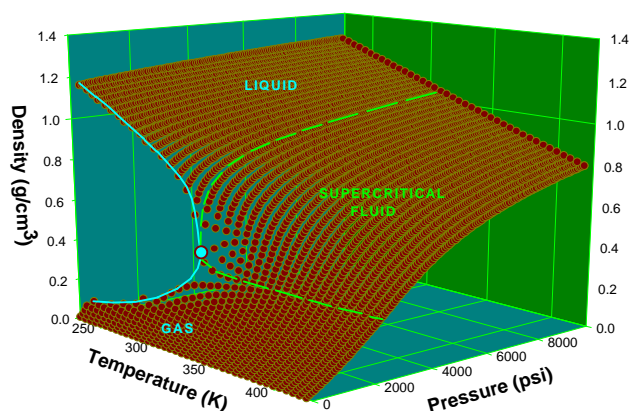


Figure 2. Pressure-temperature-density surface for pure CO₂. The critical point is shown as the solid circle.

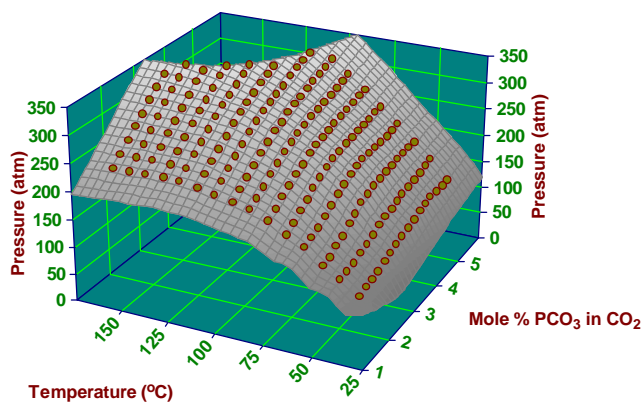


Figure 3. Vapor-liquid critical surface extrapolated from data given in [3]. The PCO₃-CO₂ mixture is single-phase at all conditions above the surface.

PMMA-based photoresist (RISTON T168). On the basis of this finding, and the fact that PCO₃ is not expected to adversely affect thin-film metallizations, we investigated this compound as a supercritical-fluid co-solvent, dissolved in carbon dioxide, for its ability to remove photoresists currently used by the Hewlett-Packard Company.

PCO₃ is an environmentally-friendly solvent, having no Personal Exposure Limit. It is non-flammable, non-toxic, biodegradable, and has a low vapor pressure.[4,5] It is readily available in high purity and in large quantities. As a co-solvent, PCO₃ is completely miscible with high-pressure CO₂, Figure 3.

The Supercritical CO₂ Resist Removal (SCORR) process involves a 5 vol.% propylene carbonate in CO₂ solvent mixture, applied in a pulsed mode. Figure 4 shows a schematic drawing of the experimental assembly constructed for the present experiments.

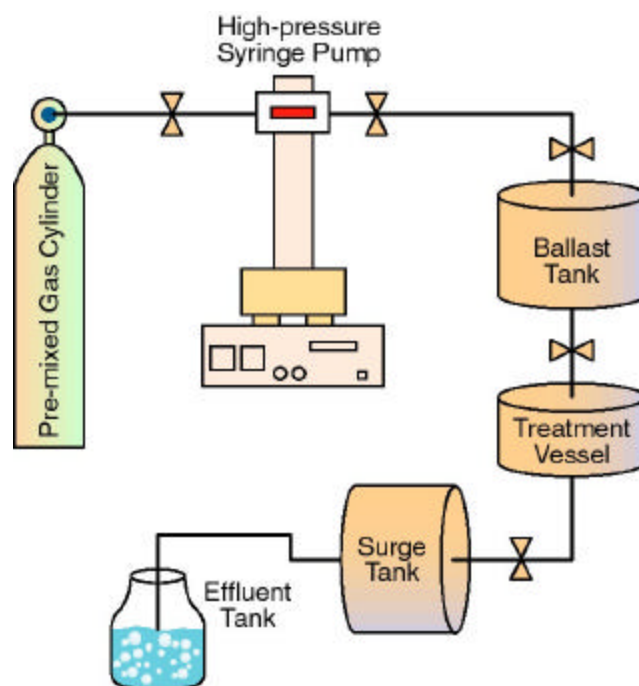


Figure 4. Schematic drawing of the SCORR treatment system.

Samples of GaAs and GaP wafers covered with positive (AZ-4330) photoresist, as well as Si wafer samples with Al, Ti-Pt, Ti-W and In-Sn oxide metallizations covered with positive photoresist (AZ 4330) were supplied by Hewlett Packard. Column 1 in Table 4 lists the four types of metallization systems evaluated in this work. Each wafer was scribed into ½-inch square samples for use in the SCORR treatment system.

The SCORR solvent is supplied by a pre-mixed, compressed gas cylinder. This cylinder feeds a high-pressure syringe pump, which supplies high-pressure, ambient-temperature SCORR solvent for a ballast tank and treatment vessel. The ½-inch square sample is centrally mounted inside the treatment vessel.

The initial conditions for the ballast tank and treatment vessel are 1600 psi and 50°C and 1100 psi and 50°C, respectively. Once the ballast tank and treatment vessel are brought to their initial conditions, a valve leading from the ballast tank to the treatment vessel is opened, allowing the solvent mixture to flow into the vessel and onto the sample surface. This flow, directed by a nozzle, continues for several seconds, until the pressures in the tank and vessel equilibrate (the final pressure of the treatment vessel rising to about 1400 psi). Subsequently, a needle valve leading from the treatment vessel to a surge tank is opened until the treatment vessel pressure drops back to 1100 psi. The surge tank is maintained at atmospheric pressure and empties into an effluent tank to retain the solvent and the spent photoresist for subsequent analysis.

While the treatment vessel de-pressurizes to 1100 psi, the ballast tank is re-pressurized to 1600 psi. This pressurization/de-pressurization cycle is repeated three times, applying the SCORR solvent in three separate pulses. Following completion of the third treatment cycle, the PCO₃ source is valved-off, and a pure CO₂ “rinse and dry” is applied to the treated sample, to remove all residual solvent and particulates. The sample is then removed from the treatment vessel and analyzed for residual photoresist.

Nuclear Reaction Analysis (NRA)

Nuclear Reaction Analysis (NRA) was used to evaluate the degree of removal of photoresist from the treated Si wafers. NRA is a rapid (< 15 min.) analytical

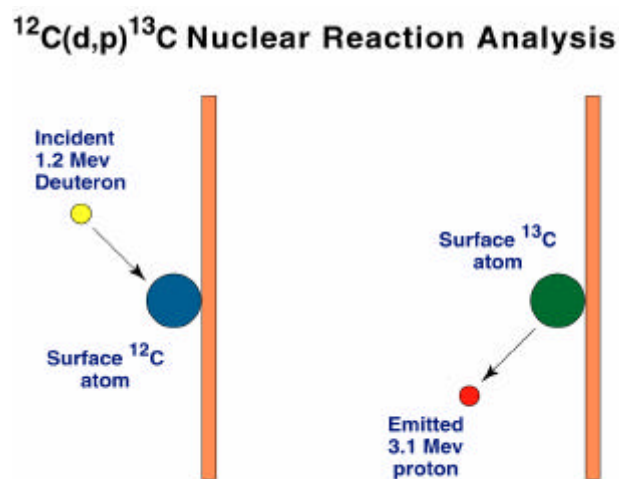
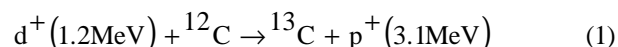


Figure 5. Schematic illustration of a ¹²C(d,p)¹³C Nuclear Reaction Analysis (NRA) measurement.

method which probes a relatively large surface area ($\approx 10 \text{ mm}^2$). The method provides a high degree of sensitivity to carbon (the main component of the resists), and is non-destructive both to the substrate and to the metallizations. As a result, we are able to obtain high-precision, quantitative data on residual carbon concentration at the sample surface, while preserving the samples for subsequent electron microscopy analysis.

In an NRA experiment, Figure 5, a beam of 1.2 MeV deuterons is directed onto the wafer surface. Carbon nuclei have an absorption resonance for deuterons at this energy, so that the deuterons are “absorbed”, temporarily raising the carbon nuclei to an excited-state. The carbon atoms relax by emitting a high-energy proton, which is detected. The overall nuclear reaction can be written :



where d^+ is the incident deuteron and p^+ is the emitted proton. The sensitivity of NRA is high, owing to the fact that the emitted protons are of much higher energy than the incident deuterons, so that there is inherently a very large

Table 4. NRA results for the four Si/metallization systems treated by the SCORR process.

Sample description	Experimental gross yield, Y (counts)	Experiential background (counts)	Adjusted Yield, Y ^{1,2} (counts)	(nt) $\left(\frac{\text{carbon atoms}}{\text{cm}^2} \right)$	Equivalent conc. of surface carbon atoms
Al film on Si	189	8	116 ± 14	$(1.0 \pm 0.1) \times 10^{16}$	10 monolayers
Al film on Si	194	24	105 ± 15	$(9.3 \pm 1.3) \times 10^{15}$	“
In-Sn oxide film on Si	138	7	66 ± 12	$(5.9 \pm 1.1) \times 10^{15}$	6 monolayers
Ti/W film on Si	97	5	27 ± 4	$(2.4 \pm 0.4) \times 10^{15}$	2 monolayers
Ti/W film on Si	159	4	-	-	-
Pt/Ti film on Si	74	6	3 ± 4	$(2.7 \pm 3.6) \times 10^{14}$	1/3 monolayers

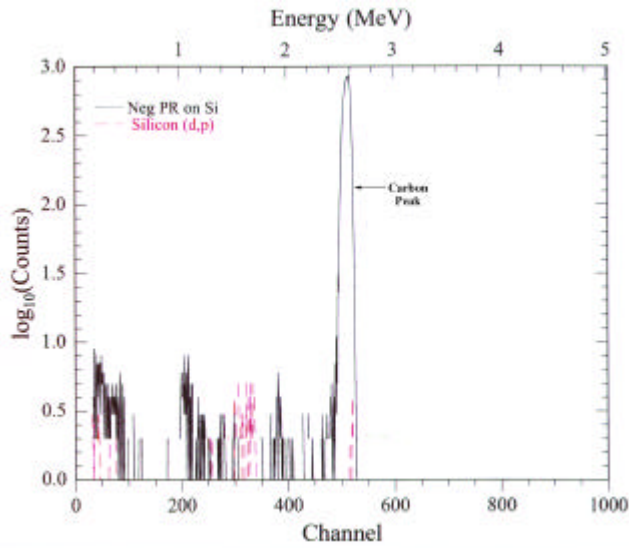


Figure 6. NRA spectra for an as-received, photoresist-coated Si sample ("Neg. PR on Si") and a virgin Si sample ("Silicon (d,p)"). Note that the ordinate is logarithmic.

signal/noise ratio.

The fundamental equation relating areal density of surface carbon nuclei to resonance absorption cross-section of carbon nuclei is

$$nt \left(\frac{\text{atoms}}{\text{cm}^2} \right) = \frac{[Y (\text{yield})]}{\left[s \left(\frac{\text{cm}^2}{\text{str}} \right) \right] [Q (\text{atoms})] [\Delta\Omega (\text{str})]} \quad (2)$$

where σ is the resonance cross section, Y is the experimental yield (in detected number of protons for a given number of incident deuterons), (nt) is the areal density of surface carbon atoms, Q is the number of incident, singly-charged deuterons, and $\Delta\Omega$ is the solid angle of the proton detector. For the beam line and experimental procedure used in these analyses, $\Delta\Omega = 2.5 \times 10^{-3}$ str, $\sigma = 90 \times 10^{-27}$ cm², $Q = 4$ μ C. The areal density of carbon atoms, nt , is therefore related to the experimental yield (or number of detected protons), Y , by

$$\left[nt \left(\frac{\text{C atoms}}{\text{cm}^2} \right) \right] = 1.78 \times 10^{14} \cdot Y \quad (3)$$

To further enhance the experimental sensitivity, the sample is tilted, relative to the incident deuteron beam, to achieve a longer interaction, or 'path', length. For all of the results reported here, the samples were tilted at 60° relative to the incident beam, so that the right side of Eq. (3) must be multiplied by $\cos(60^\circ) = 1/2$. The experimental sensitivity, *in the absence of background*, is defined by an experimental yield of one count, $Y = 1$, so that we have

$$(nt)_{60^\circ, \min} = 8.9 \times 10^{13} \left(\frac{\text{C atoms}}{\text{cm}^2} \right) \quad (4)$$

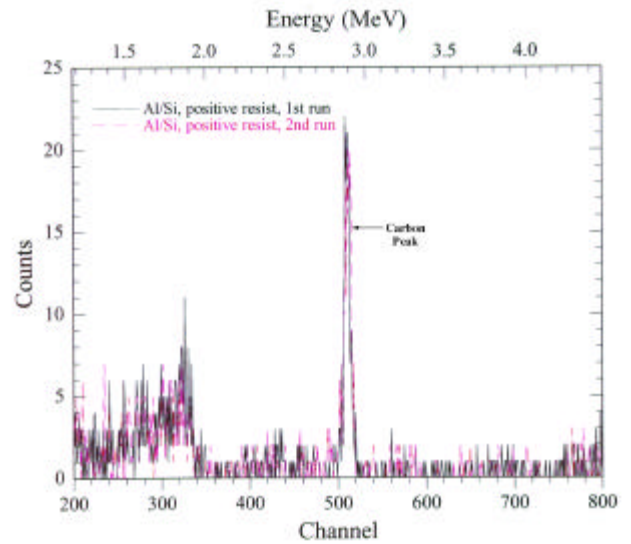


Figure 7. Duplicate NRA spectra for an Al/Si sample treated with the SCORR process. Note that the ordinate is linear.

For comparison, an areal density of $1 \times 10^{15} \left(\frac{\text{atoms}}{\text{cm}^2} \right)$ is approximately equal to a monolayer of carbon atoms.

Scanning Electron Microscopy (SEM)

Verification of photoresist removal represents only the first step of the research goal. The required second step is to demonstrate that the SCORR treatment is not destructive to the thin-film metallizations. We therefore performed electron microscopy on the 'stripped', metallized Si wafers to see if the metallizations are in any way undercut or etched. All microscopy was done on the same samples which were analyzed by NRA. No conductive coating was applied, so that low-voltage microscope operation was necessary. Further, all images were obtained with the sample tilted at 40° relative to the axis of the electron column to observe any undercutting of the metallizations.

Results - Supercritical CO₂

Nuclear Reaction Analysis (NRA)

Figure 6 shows the NRA spectra for a resist-coated Si wafer prior to SCORR treatment, along with the spectrum of a virgin Si surface. These two spectra represent the maximum and minimum surface carbon concentrations, respectively, which we can expect to see for untreated and treated samples. Figure 7 shows an Si sample with an aluminum metallization, which has been treated with the SCORR process. The NRA analysis was conducted in duplicate to demonstrate reproducibility.

Column 2 in Table 4 gives the experimental yield (number of detected protons) for the four metallized Si wafer systems (Ti/Pt, In/Sn oxide, Al, Ti/W) examined in this study, while column 3 gives the experimentally-determined background for each sample. The background is

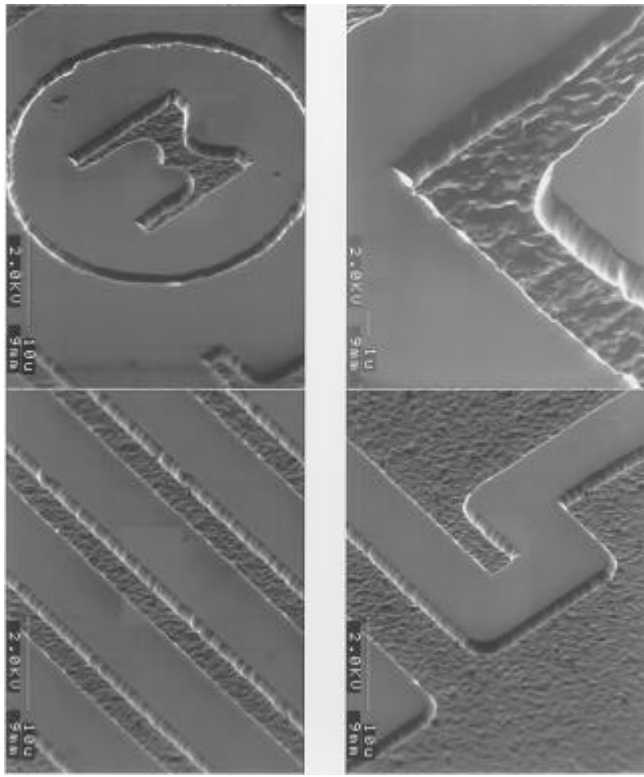


Figure 8. Composite of four electron micrographs of the SCORR-treated Al/Si sample, whose NRA spectra are shown in Figure 3.

subtracted from the experimental yield, using Eq. (4), to obtain the adjusted experimental yield, given in column 4.¹ This adjusted yield is converted, using Eq. (3), to equivalent areal density of surface carbon atoms, shown in column 5. Finally, the equivalent number of monolayers of carbon remaining on the Si wafer surface is found by dividing the quantity (nt) by

$$1 \times 10^{15} \left(\frac{\text{C atoms}}{\text{cm}^2 \cdot \text{monolayer}} \right), \text{ and is given in column 6. It}$$

is seen that the residual carbon on the wafer surfaces, after the SCORR treatment, amounts to 1-10 atomic layers. This is not considered significant since the method used to

¹ Adjusted yield is given by (gross experimental yield) - (background yield + counts due to carbon deposition), or $Y_{\text{gross}} - (Y_{\text{background}} + Y_{\text{C deposition}})$. The error in the adjusted, gross yield, $\Delta E_{\text{adj. gross}}$, is given by

$$\begin{aligned} \Delta E_{\text{adj. gross}} &= \sqrt{(\Delta E_{\text{countingstat.}})^2 + (\Delta E_{\text{Cdeposition}})^2} \\ &= \sqrt{\left[\left(\sqrt{Y_{\text{gross}}} \right)^2 + \left(\sqrt{Y_{\text{background}}} \right)^2 \right] + (3)^2} \\ &= \sqrt{(Y_{\text{gross}} + Y_{\text{background}}) + (3)^2} \end{aligned} \quad (5)$$

correct the experimental gross yield for extrinsic carbon (due to the analysis method) is only approximate, and will, if anything, be a low estimate. Further, the SCORR treatments were carried out in an open laboratory, and not in a clean-room environment and the NRA results will include carbon in the form of CO_2 left absorbed on the substrate surface during the final “rinse” step of the treatment and atmospheric CO_2 which is adsorbed during sample transfer between the treatment facility and the NRA facility.

Scanning Electron Microscopy (SEM)

Figure 8 shows a composite of four SEM micrograph of the same Al/Si sample which was treated with the SCORR process and subsequently analyzed by NRA. No etching, pitting, or undercutting are evident. A similar absence of deliterious reactions was seen for the remaining metallized samples, indicating that the supercritical fluid composition and treatment parameters are compatible with existing IC processing procedures.

Discussion - DI H_2O /Ozone

The results of our preliminary, limited evaluation indicate that this technique is very effective in removing positive photoresist. It does not work for crosslinked, fully polymerized negative resist. Also, the ozonated water process might not be compatible with all the various metallization systems used in semiconductor processing. More work will be needed to explore this area. The DIO3 TM method definitely works very well on Si, GaAs, and GaP wafers without metallizations. It seems to be an excellent technique to replace the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ mixture commonly used in silicon processing.

Discussion - Supercritical CO_2

During the course of the SCORR experimental program, we determined that pure, liquid PCO_3 used alone and pure, supercritical CO_2 used alone did not affect the resist material. Further, we found that the static application of a supercritical fluid mixture of 5 vol% PCO_3 in CO_2 , significantly softened the resist, but that removal was incomplete. It was only by combining the the PCO_3/CO_2 mixture in a pulsed-flow system could complete resist removal be achieved.

The mechanism by which the SCORR solvent removes the photoresist has not yet been determined. However, it is well known that polymeric materials can be made to swell by diffusion of CO_2 molecules and, in some instances, a significant reduction in the glass transition temperature can be produced. It is likely that such a swelling occurs, effectively softening the resist. Concomittantly, the reactive ester group of the PCO_3 acts to degrade the polymer, reducing its average molecular weight. Such a reduction promotes solubility in the supercritical fluid, facilitating its removal.

The actual treatment schedule for the samples we have examined was arbitrarily chosen, and only limited

experimentation has been devoted to process optimization. We have determined, however, that increasing the treatment temperature significantly increases the amount of photoresist softening, for a given treatment time, and would therefore be expected to significantly reduce the required, overall treatment time. Further, it must be established by electrical testing that there is no adverse effect of the SCORR treatment on pre-fabricated surface and sub-surface structures. Finally, additional work needs to be done on characterizing, on the scale of full wafers, contamination due to widely-dispersed particulates and trace metals originally present in the photoresist.

In a subsequent paper, we will present results for negative photoresist (Waycoat SC 180) coated Si wafers, as well as positive photoresist coated Si wafers which have been subjected to high-dose ion implantation.

Conclusions

The preliminary test results show that the DIO3 TM photoresist strip technique is effective in stripping positive photoresist from Si, GaAs, and GaP wafers. The process is also compatible with certain metallizations that are tolerant of the ozonated water. Additional work is needed, however, to explore this further. Overall, this technique promises : 1) significant reduction in usage of chemicals and the associated waste stream volume; (2) significant savings on chemical supplies and disposal costs, and (3) DI water volume reduction because separate, additional rinse cycles after resists stripping might become unnecessary.

Preliminary results indicate that CO₂-based supercritical fluids may also be attractive alternative solvents for photoresist stripping. Such fluids, as part of an appropriately-designed, closed-loop treatment system, have the potential to significantly reduce both waste generation and water use.

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